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(54) Deacidifying cellulosic material

(57) A method of deacidifying cellulosic material, such as books, imaged paper and other imaged material having a cellulose base, comprises treating said material with suitable alkaline particles of a basic metal oxide, hydroxide or salt dispersed in a gas or suspended in a liquid, in an amount and for a time sufficient to cause the particles to penetrate the interstices of the material, to increase the pH of the material and provide an alkaline buffer without impairing the image thereon.

SPECIFICATION

Deacidification of Cellulosic Materials

The deterioration of library materials, such as paper, books and newspapers, is a well-known and growing concern to libraries and archivists throughout the world. The causes of paper deterioration are numerous and include inherent acidity, photodegradation, oxidation, and even microbiological attack under certain conditions. These factors, combined with initial paper quality, have severely reduced the permanence of library and archival collections. A host of other phenomena such as flood, fire, vandalism, etc., certainly add to these problems; however, it is becoming generally accepted that the most insidious problem is the acidity of most paper produced in the last one hundred years.

The demand for large amounts of printing paper over the last century led to the introduction of pulp produced from wood by chemical or mechanical means. However, paper made from untreated wood pulp is too absorbent to allow sharp image imprint. Therefore, chemicals have to be added to the wood fibres during processing. These additives allow the paper to accept inks and dyes and increase paper capacity. Unfortunately, most of these chemicals are either acidic or are deposited by acidic mechanisms which initiate the slow, but relentless acidic deterioration of paper. Other contributions to the acidification of paper are supplied by man through industrial emissions of sulphur and nitrogen and carbon oxides or by natural processes such as sea salt spray. Even books or paper of neutral and alkaline character are not immune. As neighbouring papers of acidic nature degrade, volatile acids are produced which either diffuse through adjoining books or permeate the atmosphere and may ultimately acidify even the "safe or stable" books.

In order to arrest this acidic degradation, paper materials must be deacidified and provided with an alkaline reserve or buffer to retard a return to an acidic state. Currently, there are several processes in various stages of development or commercialization for deacidifying paper whether bound or unbound. Among these processes are those using volatile metal alkyls, see U.S. Patent Specifications Nos. 3,969,549 and 4,051,276, and those using volatile amines, see U.S. Patent Specifications Nos. 3,472,611, 3,771,958 and 3,703,353. Other known processes include those described in U.S. Patent Specification No. 3,676,182, which describes the treatment of cellulosic materials with alkali and alkaline earth metal bicarbonates, carbonates and hydroxides in a halogenated hydrocarbon solvent or lower aliphatic hydrocarbon, such as n-butane with an optional plasticizing agent such as ethylene glycol; in U.S. Patent Specification No. 3,676,055, which describes a nonaqueous deacidification solution for treating cellulosic materials comprising 1000 cc of 7 percent magnesium oxide (sic magnesium methoxide) in methanol and in addition 20 pounds of dichlorodifluoromethane (Freon 22); and in Canadian Patent Specification No. 911,110 which describes a deacidification solution of a 7% magnesium methoxide solution in methanol (10 parts) and a halogenated solvent or solvents (90 parts), and states that a magnesium alkoxide reacts with water in paper to form a mildly alkaline milk of magnesia, being magnesium hydroxide. Unfortunately, all of these processes suffer from one or more of a number of drawbacks that have prevented their wide-spread acceptance. These drawbacks include high cost, toxicity, complexity of treatment, residual odour, deleterious effects on certain types of paper and inks, lack of alkaline reserve, and the necessity of drying the book or other paper product to very low moisture contents before treatment.

According to the present invention there is provided a method of deacidifying material having a cellulosic base which method comprises treating said material with alkaline particles which are selected from basic metal oxides, hydroxides and salts in an amount and for a time sufficient to cause the particles to pass into the interstices of said material and increase the pH thereof, thereby to provide an alkaline buffer without impairing any image on said material.

It has now been discovered that acidic cellulosic materials can be treated with non-toxic inexpensive materials in a manner which obviates or minimizes many of the problems of the prior art including the necessity for drying the book or paper prior to treatment. This method can be used on cellulose (paper) even when such paper is imprinted and or bound. More particularly, it has been discovered that books, paper and other material having a cellulose base can be preserved by treatment with alkaline material particles of basic metal oxides, hydroxides or salts (hereinafter alternatively referred to as alkaline or basic material) in an amount and for a time sufficient to increase the acidic pH of the material and provide an alkaline buffer. Quite surprisingly, it is not necessary to neutralize the acids present within the confines of the treatment period. Rather, a basic metal oxide, hydroxide, or salt of suitable particle size is distributed through the cellulosic or paper web wherein these particles slowly stop and neutralize the acidic compounds present or produced during ageing. These basic materials are also present in sufficient amounts to buffer against reacidification by other acidic influences to which the paper may later be subjected in storage.

The alkaline materials are regularly available materials and are preferably chosen from those which are relatively non-toxic. These particles are of such a size that they do not substantially interfere with any image, are colourless, and provide good coverage. Submicron or near submicron particles are suitable as these can be suspended in a gas or inert liquid which obviates the need for solutions or solvents which contribute to many of the drawbacks of current methods. Particles of these dimensions are also tightly held within the paper matrix and do not loosen under normal use. Typical BET surface areas range from 50 to 200 m²/g which provides high probability of acid contact and interdiction.

The cellulosic 9/15/2005, EAST Version: 2.0.1.4 de, hydroxide or salt. Examples

of suitable materials are the oxides, hydroxides, carbonates and bicarbonates of the Group 1 and Group 2 metals of the Periodic Table and of zinc. Preferred are those materials in which the cation is magnesium, zinc, sodium, potassium or calcium. Particularly, preferred are the relatively non-toxic oxides, carbonates and bicarbonates of magnesium and zinc and the hydroxides of sodium, potassium and calcium.

- 5 Representative examples include magnesium oxide, magnesium carbonate, magnesium bicarbonate, zinc carbonate, zinc bicarbonate, zinc oxide, sodium hydroxide, potassium hydroxide and calcium hydroxide. Magnesium oxide is most preferred. The predominant, typically 95 to 99%, particle size is preferably in the range of from 0.01 to 0.9 micron, the average particle size is preferably in the range of from 0.2 to 0.6 micron, and most preferably is about 0.4 micron. Typical surface areas are between 50 and 200 m²/g BET and preferably about 170 m²/g. 10

- The particles can be formed by burning the elemental metal and collecting the smoke, by attrition of the preformed oxides or by calcination of the elemental salts. For example, basic magnesium carbonate can be calcined at a temperature in the range of from 450°C to 550°C to produce a polydisperse high activity magnesium oxide with an average particle size of 0.4 microns and a predominant particle size in the range of from 0.1 to 0.9 micron. 15

- The particles can be applied either in the paper making process or to the finished paper by electrostatic transfer, such as in a xerographic process, by using a dispersion thereof in a gas, or by using a suspension thereof in an inert liquid. In the case of a liquid suspension of the particles, the liquid that is used preferably possesses a high enough vapour pressure to allow its removal from the material, e.g. a book or paper, after exposure. Liquids which are well suited for this purpose are halogenated hydrocarbons. Typical materials include Dupont's Freon Fluorocarbons such as Freon 11 (trichloromonofluoromethane), Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane), and Freon 114 (1,2-dichloro-1,1,2,2-tetrafluoroethane, and Allied Chemical's Genetron 11 and 113 and mixtures thereof. The suspension is less prone to settling and/or agglomeration if a surfactant is employed to overcome surface tension and charge attraction effects. 20
- 25 Typical surfactants which can be used for this purpose include surfactants such as ICI's Solsperse 6000 and 3000 and 3M's Fluorad FC 740 and 721. Mixtures of these surfactants can also be employed. A preferred surfactant is a fluorinated alkyl ester known as Fluorad FC 740.

- The amount of surfactant and alkaline material used will depend in part on the length of treatment and the amount of deposition desired. Generally, however, the concentration of the alkaline material will be between about 0.01% and about 0.3% and that of the surfactant between about 0.005% and about 1.0%. A most preferred range for the basic material particles is between about 0.01% and about 0.2%, and a most preferred range for the surfactant is between about 0.005% and about 0.5%. 30

- In the case of the unbound or single sheets of paper, deposition may take place using a gas-supported dispersion. The gas can be, for example, air, carbon dioxide, nitrogen or argon. Active methods of deposition enhancement, such as aerosol impingement, filtering through the paper and electrostatic attraction can be used with a view to increasing the rate of deposition. Impingement of the gas-supported dispersion on the paper combined with electrostatic attraction is particularly effective. In this method, paper is placed against a charged plate and the field so created is used to attract the particles to the paper. 35

- The preferred method for bound sheet materials such as books or manuscripts is the use of a suspension in a liquid. The liquid is used not only to disperse the particles, but also to open the bound material to provide uniform treatment. By the use of spray nozzles or motion imparted to the bound material while submerged, pages can be easily separated and exposed to the particles. In a liquid suspension, one is able to obtain a higher concentration of particles in the treating medium and deposit the necessary amount of alkaline material in a shorter time. By the use of halogenated hydrocarbon/surfactant combinations, the stable concentration of submicron particles can be increased from 20—30 milligrams/cubic foot in a gas to 1—100 grams/cubic foot in a liquid. At the higher concentrations, one immersion in the treating medium for a few seconds will usually suffice to deposit the required amount of basic material. At the lower concentrations, two or more immersions or a longer immersion time is required to achieve the same effect. After immersion, the inert liquid is evaporated, recovered and recycled. 40
- 45

- 50 The following Examples will serve to illustrate the invention. All parts and percentages are by weight, unless otherwise indicated. 50

EXAMPLE 1

- Sample imaged acidic sheets were treated with an air supported dispersion of MgO powder (average 0.4 micron particle size with a predominant particles size in the range of from 0.01 to 0.9 micron and a concentration of 25 mg/cubic foot). The sheets were hung in a glove box adapted to control the humidity at 32% and the initial temperature was 22°C. at standard atmosphere. The particles were transported to the glove box through lines connected to the exhaust of a Trost Air Mill. After a three hour exposure to the static air dispersion, the pH of the paper increased to 6.6 from an initial pH of 4.4 and the image was not impaired. 55

EXAMPLE 2

- 60 Three sample imaged acidic sheets with a pH of 4.3 were dried in an oven at 50°C for one hour and then placed in a glove box under the conditions described in Example 1. Then a magnesium oxide dispersion in air as described in Example 1 was pumped into the box, and a container of warm water (40°C) was uncovered. The relative humidity went from 34 to 94% in ten minutes and the water container was closed 60

after ten minutes and the dispersion treatment was discontinued after 1 1/2 hours. The humidification treatment of the paper increased the deposition rate by more than two fold over that in Example 1. The sample sheets facing the dispersion had a pH ranging from 7.2 to 8.7.

EXAMPLE 3

- 5 A sheet of imaged acidic book paper (pH 4.0) was placed in contact with the charged sphere of an electrostatic generator (WINSO Model N 100-v). A stream of dispersed particles as described in Example 1, was directed against the paper for approximately 5 seconds. The pH of the paper after exposure was 8.5, and the image was not impaired.

EXAMPLE 4

- 10 A liquid treating suspension was prepared by adding 3.2 g (0.20%) of MgO (prepared by calcining basic hydromagnesite at 500°C for 3 hours) to 1000 ml. of Allied Chemical's Genetron—113 containing 0.78 g (0.05%) of 3M's Fluorad FC 740 surfactant. This suspension was used to treat single sheets of imaged acidic book paper by submerging each sheet into the suspension for 20 seconds. The sheets were then air-dried. These sheets (40) along with an equal number of untreated sheets were subjected to accelerated ageing according to TAPPI standard T 453 m-49 for up to 28 days. After samples were removed from the oven, the folding endurance test values of the paper were determined by using an MIT folding endurance tester (TAPPI standard T 511 su-69). The pH values were determined with a flat probe electrode according to TAPPI standard T 529 pm-74. The results obtained were as follows:

Accelerated Ageing Tests at 105°C Effect on M.I.T. Fold Endurance and pH

| Time in Days at 105°C | Untreated | | Treated | |
|--------------------------|-----------|-----|---------|-----|
| | Fold | pH | Fold | pH |
| 0 | 108 | 6.4 | 105 | 9.4 |
| 14 | 43 | 6.0 | 97 | 8.1 |
| 28 | 7 | 5.4 | 35 | 8.2 |

Note: Fold endurance is the number of double folds under a 0.5 Kg. tension before failure. Paper is considered brittle and unusable at 5 or less folds.

- This paper was from a book 37 years old. The only method presently available to determine the effects of treatment is to subject the paper to some form of accelerated ageing, in this case dry heat, and directly compare the strength retention of treated and untreated samples as shown above. The increase in life expectancy can be estimated by converting the folding endurance test values to logarithmic values and computing the regression equations of the treated and untreated paper with respect to time of accelerated ageing. Then the slopes of the resultant equations are directly compared. When this method was applied to the data above, the life expectancy of the treated paper was increased two and one-half times over its untreated counterpart.

EXAMPLE 5

- 40 The liquid suspension prepared in Example 4 was used on a newer book (age six years) with a much higher initial fold endurance. Paper taken from this book had an average pH of 5.0. After treatment as described in Example 4, the treated paper had an average pH of about 9.0. The results of an accelerated ageing test are shown below:

Accelerated Ageing Tests—Effect on M.I.T. Fold Endurance
105°C. 70°C. Sat'd R.H.

| Exposure Time Days | Unt'd | Trt'd | Unt'd | Trt'd |
|-----------------------|-------|-------|-------|-------|
| 0 | 1656 | 1656 | 1406 | 1390 |
| 7 | 281 | 498 | 933 | 1160 |
| 14 | 19 | 149 | 619 | 969 |
| 21 | 2 | 45 | 410 | 809 |

The accelerated ageing at 70°C in a water-saturated atmosphere was done to show the effects of moisture during exposure. Although the paper lost strength slower at the moist conditions, probably due to the lower temperature, acidic hydrolysis was probably enhanced. This was indicated by the pH decreases before and after exposure. The pH of the untreated paper dropped from 5.0 to 4.5 after 28 days in the dry oven, but fell to 3.7 under moist conditions. The treated samples remained about pH 9.0 in the dry oven, but fell to pH 6.6 in the moist oven after 28 days. These results indicate an increase of almost twofold in expected shelf life by dry oven ageing and somewhat more than that by moist oven ageing. Samples were removed after treatment and again after 14 days of dry oven exposure and measured for brightness. This was done when it was noticed that the treated samples appeared much whiter than the untreated samples after dry oven exposure. The brightness measurements were taken according to TAPPI standard T 452. The untreated paper fell in brightness from an average of 73.7 to 65.6, about 12%, that of the treated samples fell from 74.4 to 69.5, about 7%.

EXAMPLE 6

A 30-gallon capacity tank was filled with 20 gallons of treating suspension as described in Example 4. A bound manuscript (average pH 3.9) characterised as having a strong binding was placed with its spine against the angle of a V-shaped metal tray (angle 90 degrees). The assembly was weighted and lowered vertically (book spine perpendicular to the tank bottom) into the suspension. The bottom edge of the book block was approximately an inch above the tank bottom. A low impact, wide deflection, flat pattern spray nozzle was directed to spray downwards against the top edge of the book. The flow rate was one and one-half gallons per minute. The effect of the spray fanned the pages of the book very evenly. After five minutes, the book was removed and placed into a vacuum oven. The chamber was evacuated for 45 minutes during which time almost 100% of the fluorocarbon liquid was recovered in a refrigerated trap. Several random pH measurements on the book indicated values from 8.5—8.7. An indicator, bromocresol purple, was brushed on several pages and showed that the method used results in excellent uniformity with no image impairment.

EXAMPLE 7

The tank used in Example 6 was filled with 20 gallons of a suspension consisting of 0.3 grams (0.02%) of submicron magnesium oxide with 0.15 grams (0.01) of Fluorad FC 740 surfactant per litre. A bound volume (average pH 4.1) characterised as having a weak binding was secured to the same V-shaped tray as described in Example 5. The assembly was lowered into the suspension with the foreedge of the book pointed up. After allowing the book to separate for three minutes, the book was gently moved up and down in the suspension for an additional two minutes. Before removing the book, one cover was freed and the assembly was rotated 45 degrees in a direction opposite from the free edge. As the volume was withdrawn from the suspension, the book closed freely with little or no stress applied on the binding. The pH after air drying varied from 6.1 to 7.3 with no image impairment.

While the invention has been illustrated with the use of MgO, other alkaline material can be used in similar or like amounts. Similarly, other surfactants and inert volatile liquids for the dispersions may be used.

CLAIMS

1. A method of deacidifying material having a cellulosic base which method comprises treating said material with alkaline particles which are selected from basic metal oxides, hydroxides and salts in an amount and for a time sufficient to cause the particles to pass into the interstices of said material and increase the pH thereof, thereby to provide an alkaline buffer without impairing any image on said material.
2. A method according to Claim 1, wherein said alkaline particles have a predominant particle size in the range of from 0.01 to 0.9 micron and a surface area in the range of from 50 to 200 m²/g BET.
3. A method according to Claim 2, wherein said particles are dispersed in an inert gas.
4. A method according to Claim 3, wherein deposition of said particles in the material is enhanced by aerosol impingement, by filtering through the material or by electrostatic attraction.
5. A method according to Claim 4, wherein the deposition of said particles is enhanced by aerosol impingement and wherein the aerosol is formed of the alkaline particles in a gas.
6. A method according to Claim 5, wherein said gas is selected from air, carbon dioxide, nitrogen and argon.
7. A method according to Claim 1, wherein said particles are dispersed in an inert liquid.
8. A method according to Claim 7, wherein said inert liquid comprises a halogenated hydrocarbon.
9. A method according to Claim 7 or 8, wherein said inert liquid includes a surfactant.
10. A method according to any one of Claims 1 to 9, wherein the alkaline particles have an average particle size in the range of from 0.2 to 0.6 micron.
11. A method according to any one of Claims 1 to 10, wherein the particles comprise magnesium oxide.
12. A method according to any one of Claims 1 to 10, wherein the particles comprise a salt selected from magnesium carbonate, zinc carbonate, sodium carbonate, potassium carbonate, calcium carbonate, sodium hydroxide, 9/15/2005, EAST Version: 2.0.1.4

13. A method according to Claim 3 or to any one of Claims 4 to 12 when appendant to Claim 3, wherein the alkaline particles are applied at high humidity.
14. A method of deacidifying books, imaged paper and other imaged material having a cellulose base, which method comprises treating said books, imaged paper and other imaged material with alkaline particles which are selected from basic metal oxides, hydroxides and salts, suspended in an inert liquid, in an amount and for a time sufficient to increase the pH of the material and provide an alkaline buffer without impairing any image thereon, said liquid comprising a halogenated hydrocarbon and a surfactant. 5
15. A method according to Claim 14, wherein the halogenated hydrocarbon is 1,1,2-trichloro-1,2,2-trifluoroethane.
16. A method according to Claim 14 or 15, wherein the concentration of basic metal ranges from about 0.01% to about 0.3%. 10
17. A method according to Claim 14 or 15, wherein the concentration of basic metal ranges from about 0.01% to about 0.2%.
18. A method according to any one of Claims 14 to 17 wherein the surfactant is a fluorinated alkyl ester.
19. A method according to any one of Claims 14 to 18, wherein the predominant particle size of said alkaline particles is in the range of from 0.01 to 0.9 micron. 15
20. A method according to any one of Claims 14 to 19, wherein the average particle size of said alkaline particles is in the range of from 0.2 to 0.6 microns.
21. A method according to any one of Claims 14 to 20, wherein the average surface area of the alkaline particles is in the range of from 50 to 200 m²/g BET. 20
22. A method according to any one of Claims 14 to 21, wherein the alkaline particles comprise magnesium oxide.
23. A method according to any one of Claims 14 to 21, wherein the alkaline particles comprise a salt selected from magnesium carbonate, zinc carbonate, sodium carbonate, potassium carbonate, calcium carbonate, sodium hydroxide, potassium hydroxide and calcium hydroxide. 25
24. A method according to any one of Claims 14 to 23, wherein the concentration of the surfactant is in the range of from about 0.005% to about 1.0%.
25. A method according to any one of Claims 14 to 23, wherein the concentration of the surfactant is in the range of from about 0.005% to 0.5%.
26. A method of deacidifying books, imaged paper and other imaged material having a cellulose base, substantially as described in any one of the foregoing Examples. 30

New Claims or Amendments to Claims Filed on: 16th July 1985

Superseded Claims: 1, 2, 14

New or Amended Claims:—

1. A method of deacidifying material having a cellulosic base which method comprises treating said material with alkaline particles which are selected from basic metal oxides, hydroxides and salts, which have a predominant particle size in the range of from 0.01 to 0.9 micron and a surface area in the range of from 50 to 200 m²/g BET, and which are contacted with said material in an amount and for a time sufficient to cause the particles to pass into the interstices of said material and increase the pH thereof, thereby to provide an alkaline buffer without impairing any image on said material. 35
2. A method according to Claim 1, wherein said alkaline particles have an average particle size in the range of from 0.2 to 0.6 micron and a surface area of about 170 m²/g BET. 40
14. A method of deacidifying books, imaged paper and other imaged material having a cellulose base, which method comprises treating said books, imaged paper and other imaged material with alkaline particles which are selected from basic metal oxides, hydroxides and salts, which have a predominant particle size in the range of from 0.01 to 0.9 micron and a surface area in the range of from 50 to 200 m²/g BET, which are suspended in an inert liquid, and which are contacted with said imaged material in an amount and for a time sufficient to increase the pH of the material and provide an alkaline buffer without any image thereon, said liquid comprising a halogenated hydrocarbon and a surfactant. 45

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